ELECTROCHEMICAL SENSING USING NANODIAMOND MICROPROBE

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Keywords: Nanodiamond, Sensing, Electroactive surface, Cyclic Voltammetry, Chronocoulometry.

Abstract

Boron doped *nanodiamond* microprobe with an excellent electrochemical sensing behavior has been developed. The microprobe was fabricated by plasma enhanced chemical vapor deposition (PECVD) of nanodiamond on a sharpened tungsten microprobe with trimethyl boron (TMB) as a doping source. Electrochemical behavior of the microprobe was characterized by chronocoulometry and cyclic voltammetry in a three-electrode cell compartment to detect $Fe(CN)6^{4-}$ with KCl as background. Excellent noise-free signals down to pico-ampere range have been achieved. The probe displays reversible kinetics and a high signal to background ratio with low background current without the need of surface pretreatment. There is no indication of adsorption of analytes at the nanodiamond surface. The characterization was also performed on different active areas of the electrode that demonstrated a stable increase in current density with scan rate. The general sigmoidal shape of the voltamogram indicates spherical diffusion (rate-limited) dominated reaction mechanism.

INTRODUCTION

Micropolycrystalline PECVD diamond with controlled conductivity, dimensional stability and chemical inertness is a promising electrode material for electrochemical analysis. A wide range of electrode impedance can be realized by varying electroactive area or doping conductivity of such diamond electrodes thereby achieving detection of in-vivo electrical signals and electrochemical analysis of chemical species. However, little research in this capacity has been reported utilizing nanocrystalline diamond [1]. This work reports the electrochemical behavior of boron doped nanodiamond coated tungsten microprobe in $Fe(CN)_6^{4-}$ with KCl as background analyte. The nanodiamond microprobes show negligible adsorption of species at the electroactive surface during electrochemical analysis. Nanodiamond microprobes with different electroactive areas have also been characterized for sensitivity in electrochemical analysis.

EXPERIMENTAL

Nanodiamond microprobes were fabricated by selective deposition of nanodiamond on a sharpened tungsten microprobe. Diamond deposition was in an Astex PECVD system at power 400 W, temperature 750 ˚C, and pressure 14.5 Torr, with methane/hydrogen flow rates 15/138 sccm. Boron doping of nanodiamond was achieved with TMB as the dopant source with flow rate 10 sccm. The electrode was then sealed in a glass capillary using insulating polymer with 50 μm of the nanodiamond tip exposed for electrochemical sensing. The nanodiamond microprobe was used as the working electrode for chronocoulometry [2] and cyclic voltammetry [3] in a three-electrode cell compartment.

RESULTS AND DISCUSSIONS

Three nanodiamond microprobes with different electroactive areas were fabricated. A typical optical microscope image of a sealed nanodiamond microprobe tip is shown in Figure 1. The electroactive areas of the electrodes were determined using two-step chronocoulometry and the slope obtained in equation (1) [2].

$$Slope = \frac{2nAFC\sqrt{D}}{\sqrt{\pi}} \quad (1)$$

where n is the number of electrons participating in a single transfer, A is the area of the active electrode, F is the Faraday constant, C is the concentration and D is the diffusion constant.

Figure 2 shows the two step chronocoulometry with nanodiamond microprobe in 3.9 mM $Fe(CN)_6^{4-/3-}$ in 0.1 M KCl. The intersection of oxidation and reduction components at zero axis (origin) shows that there is

negligible occurrence of adsorption at the nanodiamond surface. Figure 3 shows the CV for detection of various concentrations of $Fe(CN)_4^{4-/3-}$ in 0.1 M KCl at a scan rate of 10 mV s^{-1}. The curve displays high signal to background ratio and absence of any noticeable noise. The peak separation varies from 93 mV to 124 mV. The reversal peak ratio ($I_{p,red}/I_{p,ox}$), which varies from 0.95 to 0.96, satisfies the requirement for a redox couple. The sigmoidal shape of the voltamogram indicates rate-limited rather than diffusion limited reaction mechanism. Figure 4 shows the variation of oxidation current with various concentrations of $Fe(CN)_6^{4-/3-}$. The curve shows a linear variation of the current as the concentration of the analyte increases.

CONCLUSION

The nanodiamond microprobe is an excellent electrode for electrochemical analysis. It picks up current down to pico-amps range with noise-free signals. The immunity to adsorption at the nanodiamond surface and optimization for rate-limited reaction mechanisms makes it suitable for in-vivo and in-vitro analysis. Moreover, the variation of chemical reaction rate and current as the microprobe approaches targeted tissue in-vivo can be measured with SECM (Scanning Electrochemical Microscopy) facilitating reproducibility for applications such as neurological mapping. Details of SECM data will be included in the paper.

Figure 1. *View of nanodiamond microprobe in optical microscope*

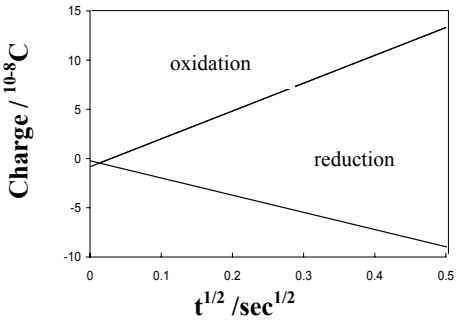

Figure 2. *Two step chronocoulometry with nanodiamond in 3.9 mM$Fe(CN)_6^{4-}$ in 0.1 M KCl.*

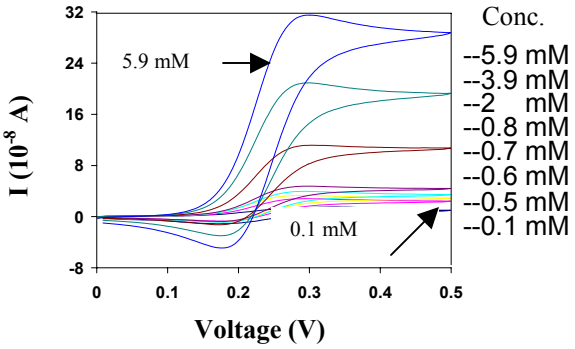

Figure 3. *Cyclic voltammogram of nanodiamond microprobe for detection of different concentrations (conc.) of $Fe(CN)_6^{4-/3-}$ in 0.1 M KCl. Scan rate = 10 mV s^{-1}*

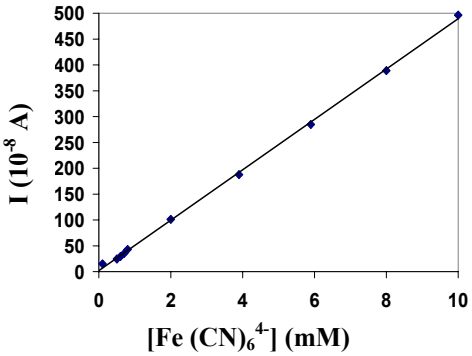

Figure 4. *The plot of oxidation current against various concentrations of $Fe(CN)_6^{4-}$ in 0.1 M KCl.*

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